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Protocol for the Collection and Analysis of Volatile POHCs (Principal Organic Hazardous Constituents) Using VOST (Volatile Organic Sampling Train)

Envirodyne Engineers, Inc., St. Louis, MO

Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

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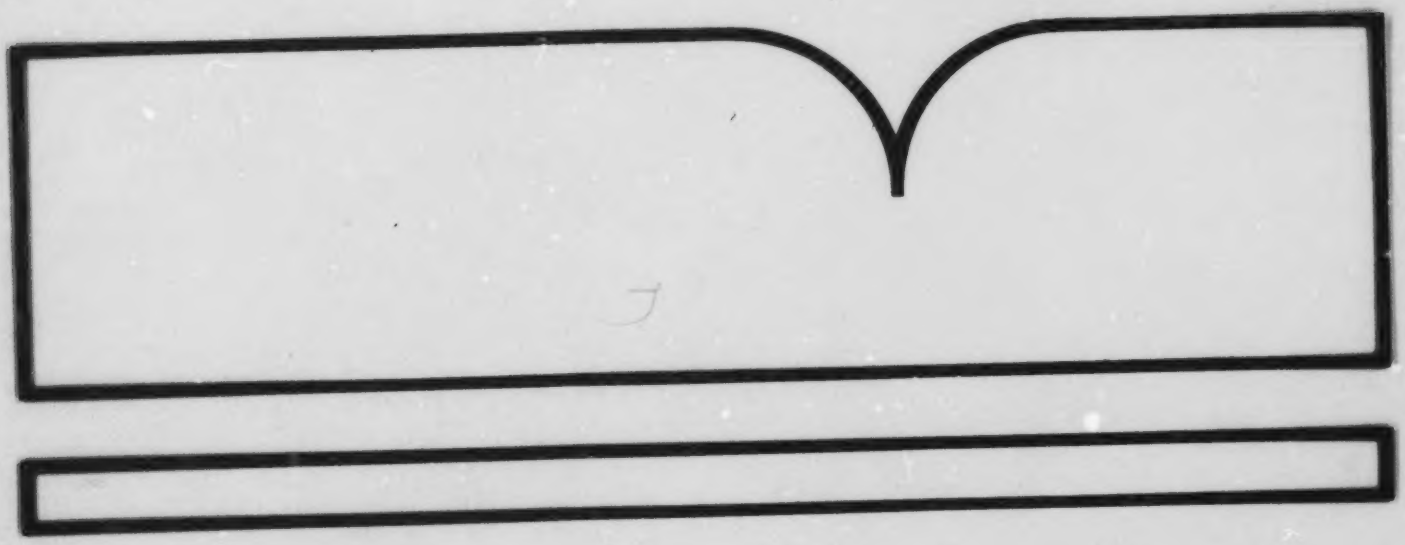

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PROTOCOL FOR THE COLLECTION AND ANALYSIS OF VOLATILE POHCs USING VOST

By

Earl M. Hansen

Envirodyne Engineers, Inc.
12161 Lackland Road
St. Louis, Missouri 63146

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EPA Project Officer: Robin M. Anderson
Technical Support Office
U. S. Environmental Protection Agency
Industrial Environmental Research Laboratory
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16. ABSTRACT The document is a state-of-the-art operating protocol for sampling and analysis of volatile organic constituents of flue gas from hazardous waste incinerators or other similar combustor systems using the Volatile Organic Sampling Train (VOST). It is intended to be used for guidance by personnel of the regulatory groups, personnel associated with engineering research and development, and the regulated community. The document is in two parts. Part A describes the key components of the train, the procedures for preparing the sorbent materials, and procedures for sample collection using the VOST. Part B describes the procedures for analyzing VOST sorbent cartridges for volatile principal organic hazardous constituents (POHCs) using purge-trap-desorb gas chromatography/mass spectrometry (P-T-D GC/MS). Quality control procedures are presented in both parts.

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Flue Gases		Stationary Sources	21B	11G
Organic Compounds	Toxicity	VOST	07C	06T
Analyzing			14B	
Sampling				
Collection			14G	

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NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

This report has been produced by EPA's Office of Research and Development as part of ongoing studies in support of engineering research and regulatory programs including EPA's Office of Solid Waste, EPA Regional Offices, and appropriate State Agencies. The document contains state-of-the-art operating protocols for sampling and analysis of volatile organic constituents of flue gases from hazardous waste incinerators or other similar combustor systems. It is intended as a reference to be used for guidance by personnel of the regulatory groups, personnel associated with engineering R&D, and the regulated community.

Publication of this report does not constitute official designation as an EPA method. Official test methods for hazardous waste related programs are published in SW-846 "Tests Methods for Evaluating Solid Waste," as well as in the Federal Register.

Frank T. Princiotta
Director
Industrial Environmental Research Laboratory

CONTENTS

	Page
Foreword	iii
Figures	vi
Acknowledgements	vii
Introduction	viii
Abstract	ix
PART A: SAMPLE COLLECTION FOR THE DETERMINATION OF EMISSIONS OF VOLATILE ORGANIC COMPOUNDS FROM HAZARDOUS WASTE INCINERATORS	A-1
1. Scope of Applicability	A-1
2. Summary of Method	A-3
3. Precision and Accuracy	A-5
4. Interferences	A-6
5. Apparatus	A-7
5.1 Volatile Organic Sampling Train	A-7
5.2 Probe	A-7
5.3 Isolation Valve	A-10
5.4 Condensers	A-10
5.5 Sorbent Cartrides	A-10
5.6 Impinger	A-15
5.7 Metering Systems	A-15
5.8 Sample Transfer Lines	A-16
6. Reagents and Materials	A-16
6.1 2,6-Diphenyline Oxide Polymer Tenax (35/60 Mesh)	A-16
6.2 Charcoal (SKC Lot 104 Petroleum Base or equivalent)	A-17
6.3 Viton O-Ring	A-18
6.4 Glass Tubes/Condensers	A-18
6.5 Metal Parts	A-18
6.6 Silica Gel	A-18
6.7 Crushed Ice	A-19
6.8 Water	A-19
6.9 Glass Wool	A-19
6.10 Nitrogen	A-19
7. Assembly and Conditioning of VOST Sorbent Cartridges	A-19
7.1 Introduction	A-19
7.2 Assembly of Tenax Cartridges	A-20
7.3 Assembly of Tenax/Charcoal Cartridges	A-21
7.4 Sorbent Cartridge Quality Assurance	A-22
8. Sample Collection Procedure	A-23
8.1 Pretest Preparation	A-23
8.2 VOST Assembly	A-24
8.3 Leak Checking	A-24
8.4 Sample Collection	A-26
8.5 Field, Trip, and Laboratory Blanks/Aqueous Field Blank	A-28

CONTENTS
(Continued)

		Page
PART B:	PROTOCOL FOR ANALYSIS OF SORBENT CARTRIDGES FROM VOLATILE ORGANIC SAMPLING TRAIN	B-1
1.	Scope and Applicability	B-1
2.	Summary of Method	B-2
3.	Precision and Accuracy	B-4
4.	Apparatus	B-4
4.1	Thermal Desorption Unit	B-4
4.2	Purge and Trap Unit	B-5
4.3	GC/MS System	B-5
5.	Reagents	B-6
5.1	Reagent Water	B-6
5.2	Analytical Trap Reagents	B-7
5.3	Stock Standard Solution	B-8
5.4	Secondary Dilution Standards	B-8
5.5	Bromofluorobenzene (BFB) Standard	B-8
5.6	Deuterated (d_6) Benzene Standard	B-8
6.	Calibration	B-9
6.1	Assembly of P-T-D Device	B-9
6.2	Internal Standard Calibration Procedure	B-9
7.	Quality Control	B-12
8.	Sample Collection, Preservation, and Handling	B-15
9.	Daily GC/MS Performance Tests	B-15
10.	Sample Desorption and Gas Chromatography	B-16
11.	Aqueous Condensate	B-17
12.	Qualitative Identification	B-17
13.	Calculations	B-18
14.	Method Performance	B-21
REFERENCES (For A and B)		B-22

FIGURES

No.		Page
1	Schematic of Volatile Organic Sampling Train	A-8
2	Volatile Organic Sampling Train (I/O Cartridge Design)	A-9
3	I/O Sorbent Trap Assembly, Volatile Organic Sampling Train (VOST)	A-12
4	Inside/Inside VOST Cartridge	A-13
5	VOST Field Data Sheet	A-25
6	Schematic Diagram of Trap Desorption/ Analysis System	B-3

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INTRODUCTION

The Resource Conservation and Recovery Act (RCRA) requires that owners/operators of facilities which treat hazardous waste by incineration ensure that the incinerators are operated in a manner which does not endanger human health or the environment (1,2). The Code of Federal Regulation, Title 40, Part 264, requires that a destruction and removal efficiency (DRE) of 99.99 percent be achieved for each principal organic hazardous constituent (POHC) designated in the Trial Burn Permit (3). The DRE standard implicitly requires sampling and analysis to quantify POHCs in the waste feed material and stack gas effluent. The "Sampling and Analysis Methods for Hazardous Waste Combustion" manual (method manual) provides information on methods that are applicable for collection and analyses of POHCs in process streams of hazardous waste incinerator units (4).

The methods manual identifies three possible methods for the collection of volatile organics (those with boiling points <100°C). The methods include bag, glass bulb, and the Volatile Organic Sampling Train (VOST). Evaluation of the bags and bulbs indicates that these sampling systems are subject to a number of technical problems. The most important of these problems is the inadequate sensitivity for detection of POHCs present in low concentrations.

The VOST provides increased sensitivity to low level concentration of volatile POHCs due to the ability to concentrate the gaseous effluent. The results of laboratory evaluation and field application of the VOST have shown that it provides sufficient sensitivity to permit calculation of a DRE equal to or greater than 99.99 percent for volatile POHCs which are present in the waste feed at 100 µg/g (5).

The methods manual identifies the VOST as a suitable sampling system for volatile organics and includes a paper describing the VOST (5). A detailed protocol was not included in the methods manual due to the fact that this is outside the scope of the document. Since the VOST is new technology, it is felt a protocol should be made available.

The purpose of this protocol is to provide a standard operating procedure to users of the VOST in the collection and analysis of samples for volatile POHCs in the gaseous effluents of hazardous waste incinerators or gaseous effluents of hazardous waste co-fired combustion processes. The protocol is presented in two parts. Part A describes the key components of the VOST train, and the procedure for sample collection using VOST. Part B describes the procedures for analysis of VOST sorbent cartridges for volatile POHCs using purge-trap-desorb gas chromatography/mass spectrometry (P-T-D GC/MS).

ABSTRACT

This document provides a state-of-the-art operating protocol for sampling and analysis of volatile organic constituents of flue gas from hazardous waste incinerators or other similar combustion systems using the Volatile Organic Sampling Train (VOST). It is intended to be used for guidance by personnel of the regulatory groups, personnel associated with engineering Research and Development, an dthe regulated community.

The VOST is designed to extract and concentrate volatile organic compounds (boiling ≤100°C) from stack gas effluents. The concentrated organics are analyzed by procedures chosen to be compatible with the VOST in order to obtain flue gas concentration levels. This information is necessary to perform destruction and removal efficiency (DRE) calculations for incinerator operations. The results of laboratory evaluation and field use of the VOST have shown that the VOST provides sufficient sensitivity to permit calculation of a DRE equal to or greater than 99.99 percent for volatile organics present in the waste feed at 100 µg/g.

The VOST is directly applicable to organic compounds with boiling points of 30° to 100°C. Many organic compounds with boiling points less than 30°C, or with boiling points in the 100° to 150°C range, may also be collected and analyzed by this method. Field application of the VOST for compounds with boiling points outside the 30° to 100°C range should be attempted only after laboratory evaluation of the collection and recovery efficiencies of the specific compounds.

The document is presented in two parts. Part A describes the key components of the train, the procedures for preparation of the sorbent materials, and procedures for sample collection using the VOST. Part B describes the procedures for analysis of VOST sorbent cartridges for volatile principal organic hazardous constituents (POHCs) using purge-trap-desorb gas chromatography/mass spectrometry (P-T-D GC/MS). Quality control procedures are presented in both Sections A and B.

PART A

SAMPLE COLLECTION FOR THE DETERMINATION OF THE EMISSIONS OF VOLATILE ORGANIC COMPOUNDS FROM HAZARDOUS WASTE INCINERATORS

1. SCOPE AND APPLICABILITY

1.1 This protocol describes the method of collection of volatile principal organic hazardous constituents (POHCs) from the stack gas effluents of hazardous waste incinerators. This method is applicable to compounds with boiling points in the range of 30° to 100°C. If the boiling point of a POHC of interest is less than 30°C, the POHC may breakthrough the sorbent under the conditions of the sample collection procedure. Field application for POHCs of this type should be supported by laboratory data which demonstrates the efficiency of a volatile organic sampling train (VOST) to collect POHCs with boiling points less than 30°C (Part B, Section 7). The collection of organic compounds with low boiling points may require using reduced sample volumes collected at flow rates between 250 and 500 milliliters per minute (ml/min). Many compounds which boil in the range of 100° to 150°C (e.g., chlorobenzene, ethylbenzene, tetrachloroethane, bromoform) may be efficiently collected and analyzed using this method. VOST recovery efficiencies for these compounds should also be demonstrated, where necessary, by laboratory data of the type described above (Part B, Section 7).

1.2 This method is applicable to the determination of volatile POHCs in the stack gas effluent of hazardous waste incinerators and other similar combustion systems. This method is designed for use in calculating the destruction and removal efficiency (DRE) for the volatile POHCs. The method provides sufficient precision and accuracy to enable the calculation of DRE values equal to or greater than 99.99 percent (5).

1.3 The sensitivity of this method is dependent upon the level of interferences in the sample and the presence of detectable levels of volatile POHCs in blanks. The target detection limit of this method is 0.1 micrograms per cubic meter ($\mu g/m^3$) [0.1 nanograms per liter (ng/l)] of flue gas which permit calculation of a DRE equal to or greater than 99.99 percent for those volatile POHCs which may be present in the waste feed stream at 100 parts per million (ppm). Laboratory development data (5) have demonstrated a range of 0.1 to 100 $\mu g/m^3$ (0.1 to 100 ng/l) for selected volatile POHCs.

1.4 The range of applicability for this method is limited by breakthrough of volatile POHCs on the sorbent cartridges used to collect the sample, caution should be exercised in using the VOST to collect samples from a stack gas stream in which one or more of the volatile POHCs are present in concentrations greater than 500 $\mu g/m^3$ (500 ng/l). If, for example, an incinerator uses a waste fuel containing volatile POHCs at a concentration of 50,000 to 100,000 µg/g, and the incinerator achieves a DRE of 99.99%, then

the concentration in the effluent would be 500 to 1000 µg/m^3 (500 to 1,000 ng/l), respectively. Analysis using the procedures described in Part B of this method would probably result in overloading the analytical instrumentation and therefore would not provide valid data for that particular POHC. Where the waste contains volatile POHCs at high concentrations, consideration should be given to collecting gaseous effluent samples using SLOW-VOST techniques, gas bags or evacuated glass bulbs. Further, if the waste contains volatile POHCs at high (50,000 µg/g) and low (100 µg/g) concentrations, these POHCs might not be quantifiable using only VOST. In this case, consideration should be given to either collecting gaseous effluent samples using two VOST trains (one of these trains should be operated under conditions of SLOW-VOST), or using one VOST train (SLOW-VOST) and gas bags or glass bulbs. The examples cited above may result in chromatographic interferences or instrument overloading which will invalidate the results. If this situation is anticipated, laboratory evaluation should be conducted prior to field use of the VOST (Part B, Section 7).

1.5 This method is recommended for use only by experienced sampling personnel and analytical chemists, or under close supervision by such qualified persons.

2. SUMMARY OF METHOD

2.1 A 2-hour sample of gaseous effluent is collected on cartridges using six pairs of cartridges, each pair sampling a maximum of 20 liters of gaseous effluent. The samples are collected

at a sampling flow rate of 1 liter per minute, using temperature controlled quartz or glass lined probe and a VOST. The gas stream is cooled to 20°C by passage through a water-cooled condenser and volatile POHCs are collected on a pair of sorbent cartridges. Liquid condensate is collected in an impinger placed between the two sorbent cartridges. The first sorbent cartridge (front cartridge) contains approximately 1.6 grams Tenax, and the second cartridge (back cartridge) contains approximately 1 gram each of Tenax and petroleum based charcoal (SKC Lot 104 petroleum base or equivalent, see Section 6.2.1), 3:1 by volume.

2.2 An alternative set of conditions for sample collection has been used. This method involves collecting a sample volume of 20 liters or less at a reduced flow rate. Operation of the VOST under these conditions has been referred to as SLOW-VOST. This method has been used to collect 5 liters of sample (0.25 liters/min for 20 minutes) or 20 liters of sample (0.5 liters/min for 40 minutes) on each pair of sorbent cartridges. Smaller sample volumes collected at lower flow rates should be considered when the boiling points of the POHCs of interest are below 30°C or for volatile POHCs present in high concentrations in the stack gas.

2.3 The gaseous effluent shall be sampled over a 2-hour period. This is accomplished using six pairs of Tenax and Tenax/charcoal cartridges sampling a maximum of 20 liters of gaseous effluent on each pair of cartridges. Fewer pairs of cartridges may be

required using SLOW-VOST (Section 2.2). A minimum of three pairs of Tenax and Tenax/charcoal cartridges shall be collected for SLOW-VOST sampling.

2.4 Analysis of the cartridges (described in Part B) for volatile POHCs using purge-trap-desorb gas chromatograph/mass spectrometer (P-T-D GC/MS) which is carried out by thermally desorbing each cartridge with the gas passing through a water filled purge column onto an analytical trap. The analytical trap is subsequently heated and the effluent gas passes into the GC/MS.

3. PRECISION AND ACCURACY

3.1 The results of laboratory evaluations of the VOST for selected volatile POHCs showed that the recovery of the analytes from three pairs of replicate cartridges ranged from ±50 percent of the expected value (5).

3.2 Prior to field operation of the VOST at a hazardous waste incinerator, a laboratory trial should be conducted using either selected volatile POHCs of interest or two or more of the volatile POHCs for which data are available (5). The user shall demonstrate proficiency which is within the precision and accuracy of the method (Part B, Section 7). Experienced users of VOST who have demonstrated proficiency with the VOST and can provide data which supports the applicability of the VOST for the POHCs may be exempt from this requirement. Before the VOST shall be used to

sample compounds below 30°C, the user must demonstrate through laboratory evaluations of the collection and recovery efficiencies that the accuracy and precision requirements are met (Part B, Section 7).

4. INTERFERENCES

4.1 Interferences arise primarily from background contamination of sorbent cartridges prior to or after use in sample collection. Many potential interferences can be due to exposure of the sorbent materials to solvent vapors prior to assembly and exposure to significant concentrations of volatile POHCs in the ambient air at hazardous waste incinerator sites. Benzene and toluene appear to be inherent contaminants on Tenax. This may present problems in the analysis of these compounds using VOST due to high background concentrations. To minimize this problem, the use of additional field blanks is recommended (see Section 8.5).

4.2 To avoid or minimize the low level contamination of train components with volatile POHCs, care should be taken to avoid contact of all interior surfaces or train components with synthetic organic materials (e.g. organic solvents, lubricating and sealing greases), and train components should be carefully cleaned and conditioned according to the procedures described in Sections 5, 6 and 7 of this protocol. The sorbent cartridges should be conditioned and stored in an environment free of volatile organic compounds.

5. APPARATUS

5.1 Volatile Organic Sampling Train

5.1.1 A schematic diagram of the principal components of the VOST is shown in Figure 1. A diagram of the assembled components of one version of the VOST is shown in Figure 2. The VOST consists of: a quartz or glass lined probe with a glass wool particulate plug, an isolation valve, a water cooled glass condenser with thermocouple placed at the outlet to monitor gas stream temperature (see Section 5.6.2), a sorbent cartridge containing Tenax (1.6 grams), an empty impinger for condensate removal, a second water cooled glass condenser, a second sorbent cartridge containing Tenax and petroleum based charcoal (3:1 by volume; approximately 1 gram of each), a silica gel drying tube, a calibrated rotameter, a sampling pump, and a dry gas meter.

5.1.2 The gas pressure during sampling and for leak checking is monitored by vacuum gauges which are in line with and downstream of the silica gel drying tube.

5.2 Probe

5.2.1 The probe shall be maintained at a temperature of at least 130°C in the gas stream prior to the first condenser. If one or more of the volatile POHCs boil between 130° to 150°C, the probe shall be maintained at a temperature equivalent to the boiling point of the least volatile POHC. The probe may require heating to achieve this temperature. If stack temperatures are excessively high, an air or water cooled probe may be required to

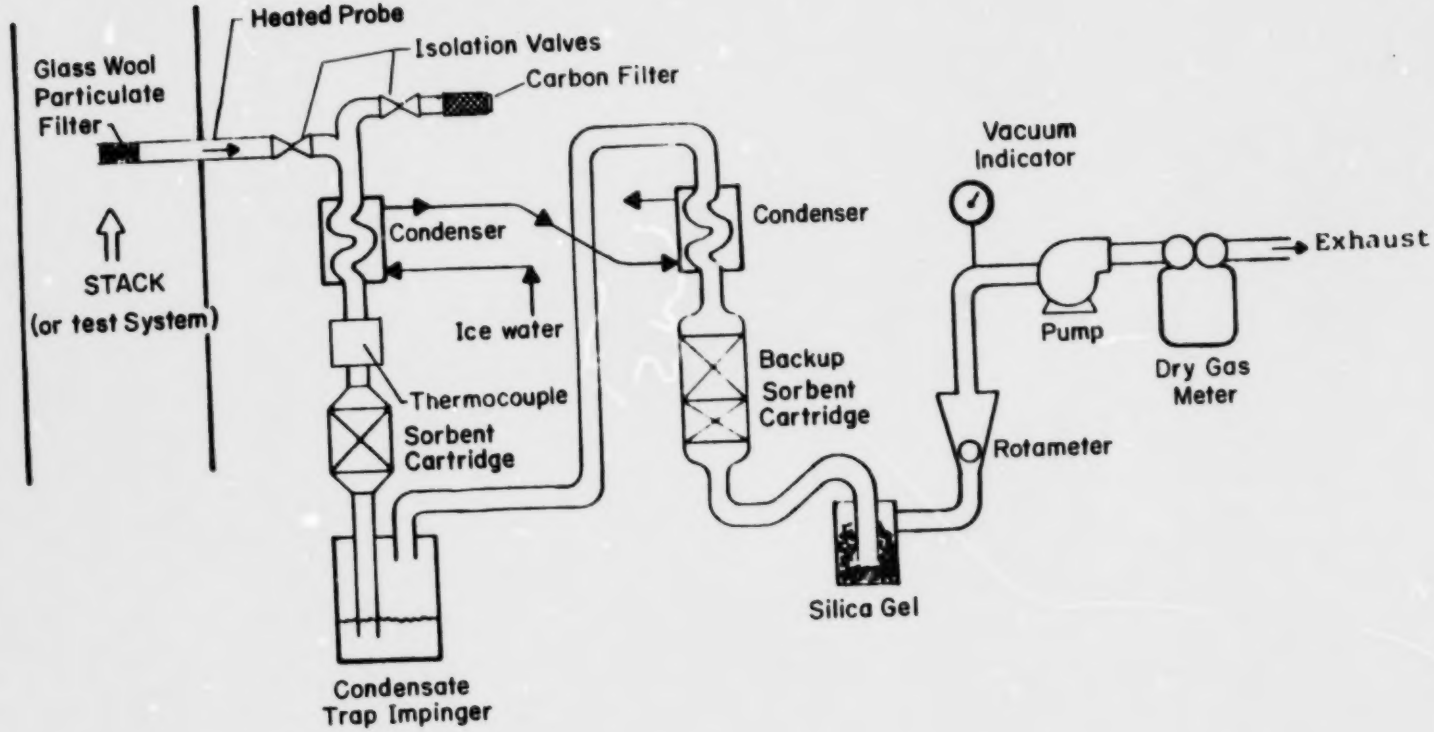


FIGURE 1
SCHEMATIC OF
VOLATILE ORGANIC SAMPLING TRAIN
(VOST)

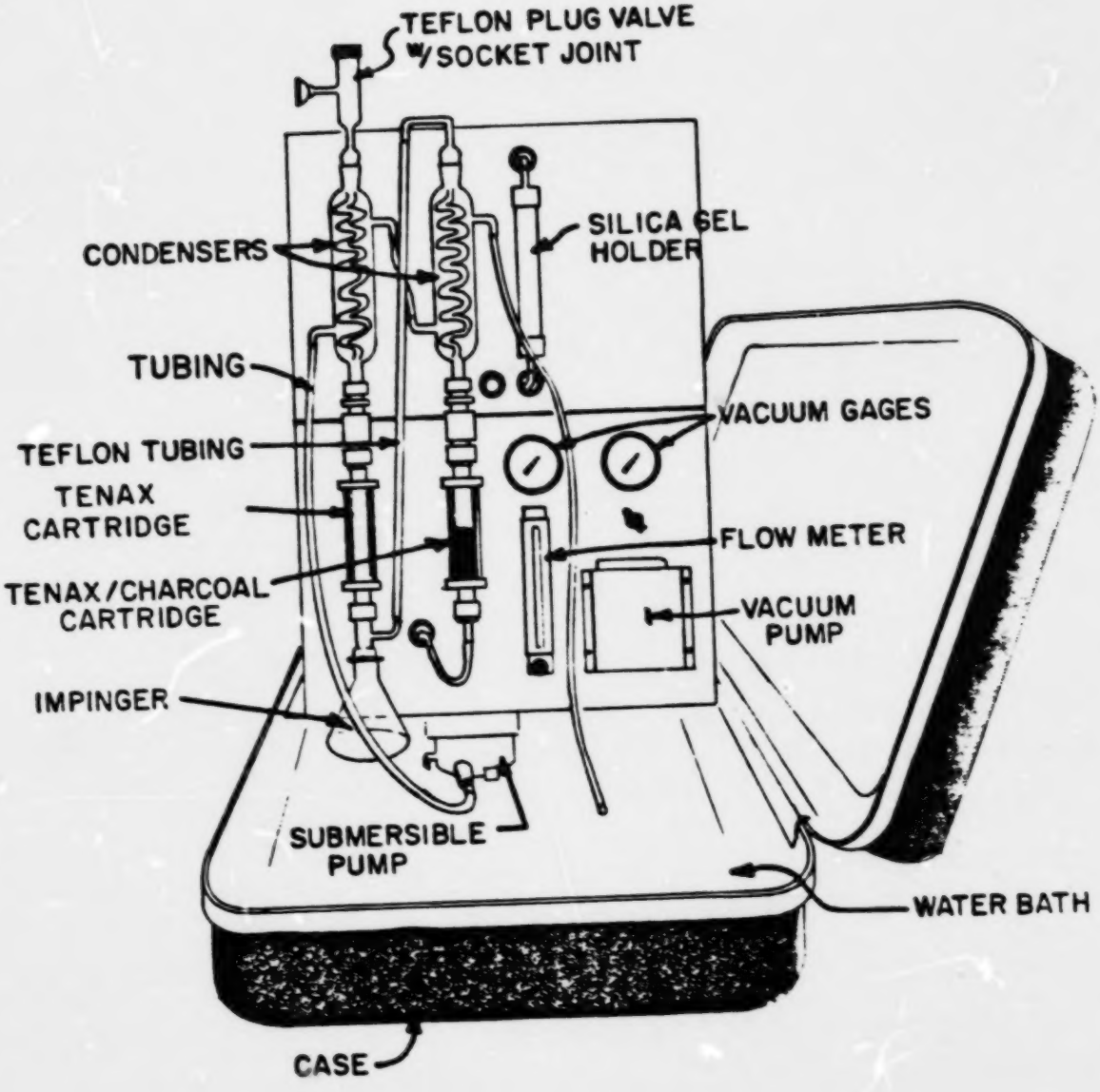


FIGURE 2

VOLATILE ORGANIC SAMPLING TRAIN
(1/0 CARTRIDGE DESIGN)

avoid damage to the probe and to achieve a temperature of 20°C at inlet to first sorbent cartridge (see Section 5.4). Isokinetic sample collection is not a requirement for the use of VOST since the compounds of interest are in the vapor phase at the point of sample collection.

5.3 Isolation Valve

5.3.1 The isolation valves must be a greaseless stopcock with a glass bore and sliding Teflon plug with Teflon wipers (Ace 8193 or equivalent). These valves are used to permit ambient air to be admitted after leak checking (Section 8.3) and for purging the probe prior to sample collection (Section 8.4).

5.4 Condensers

5.4.1 The condensers (Ace 5979-14 or equivalent) shall be of sufficient capacity to cool the gas stream to 20°C or less prior to passage through the first sorbent cartridge. The top connection of the condenser shall be able to form a leak-free, vacuum-tight seal without using vacuum sealing greases.

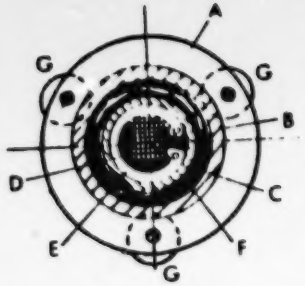
5.5 Sorbent Cartridges

5.5.1 The sorbent cartridges for the VOST are available and acceptable in either of two configurations: the inside/outside (I/O) or inside/inside (I/I) configuration. The terms I/O or I/I pertain to the instrument configuration for thermal desorption of the sorbent tubes. For the I/O design, the carrier gas contacts the inside and outside of the sorbent tubes during the desorption,

while for the I/I design, the carrier gas is directed only through the inside of the cartridge. For the I/O configuration, the cartridge is held in the VOST within an outer glass tube and in a metal carrier (Figure 3). For the I/I configuration, a single glass tube is used, with or without a metal carrier (Figure 4). In either case, the sorbent packing will be the same. The first pair of sorbent cartridges shall be packed with approximately 1.6 grams Tenax GC resin, and the second cartridge of a pair shall be packed with Tenax GC and petroleum based charcoal (3:1 by volume; approximately 1 gram of each).

5.5.2 The second sorbent cartridge shall be packed so that the sample gas stream passes through the Tenax layer first and then through the charcoal layer. Note that when sorbent cartridges are analyzed using the P-T-D GC/MS procedure described in Part B, Section 10.2, the gas flow through the sorbent cartridges during desorption is in the opposite direction from the gas flow through the sorbent cartridges during sample collection. The inlet side of each cartridge during sample collection shall be clearly identified so that it becomes the outlet side during the desorption step of the analytical procedure.

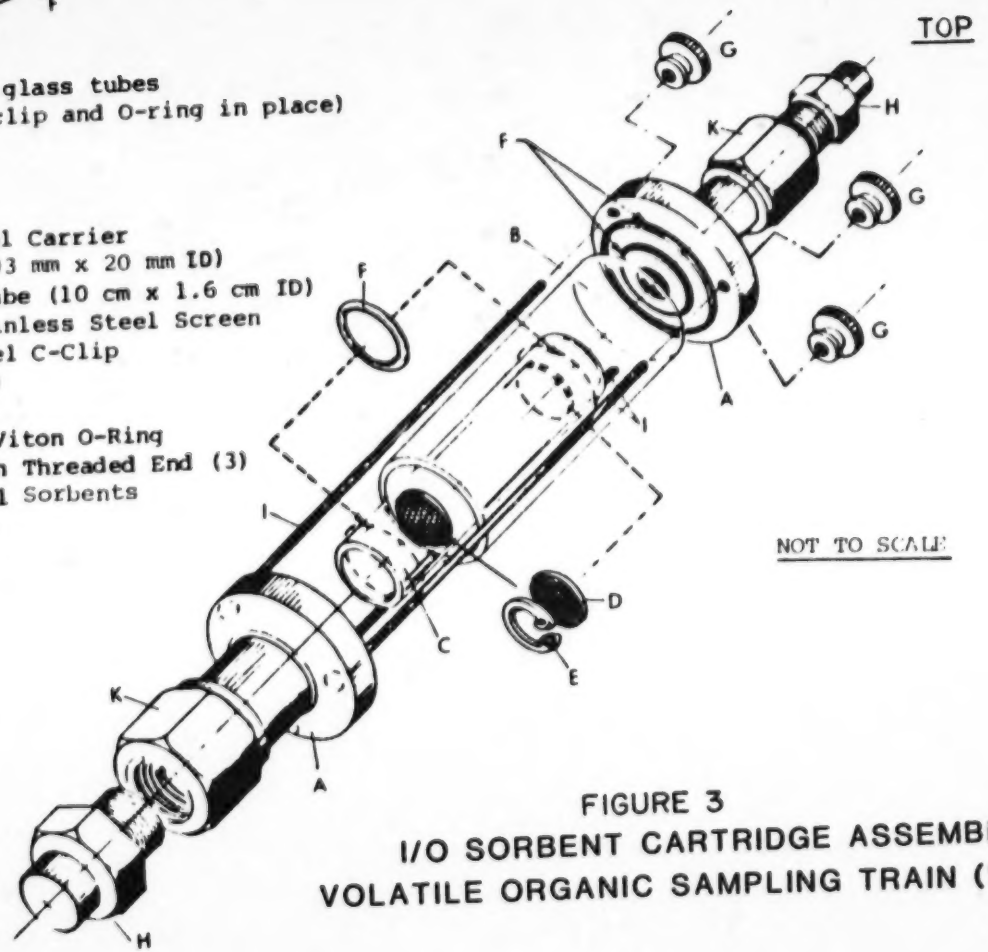
5.5.3 The sorbent cartridges shall be glass tubes with approximate dimensions of 10 centimeters by 1.6 centimeters (cm) I.D. The two acceptable designs (I/O, I/I) for the sorbent cartridge are described in further detail below.

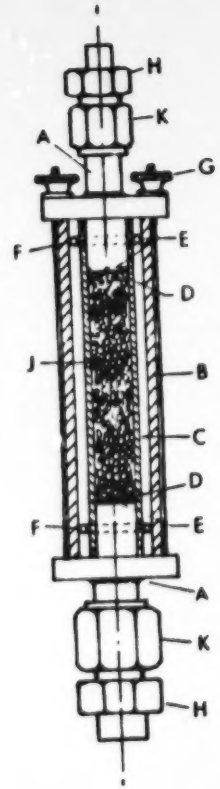


Section cut through glass tubes
(showing screen, C-clip and O-ring in place)

LEGEND

A - Stainless Steel Carrier
B - Glass Tube (103 mm x 20 mm ID)
C - Small Glass Tube (10 cm x 1.6 cm ID)
D - Fine Mesh Stainless Steel Screen
E - Stainless Steel C-Clip
F - O-Ring (Viton)
G - Nuts (3)
H - End Cap with Viton O-Ring
I - Metal Rod with Threaded End (3)
J - Tenax/Charcoal Sorbents
K - Cajon Fitting





Assembled Trap
NTS

FIGURE 3
I/O SORBENT CARTRIDGE ASSEMBLY
VOLATILE ORGANIC SAMPLING TRAIN (VOST)

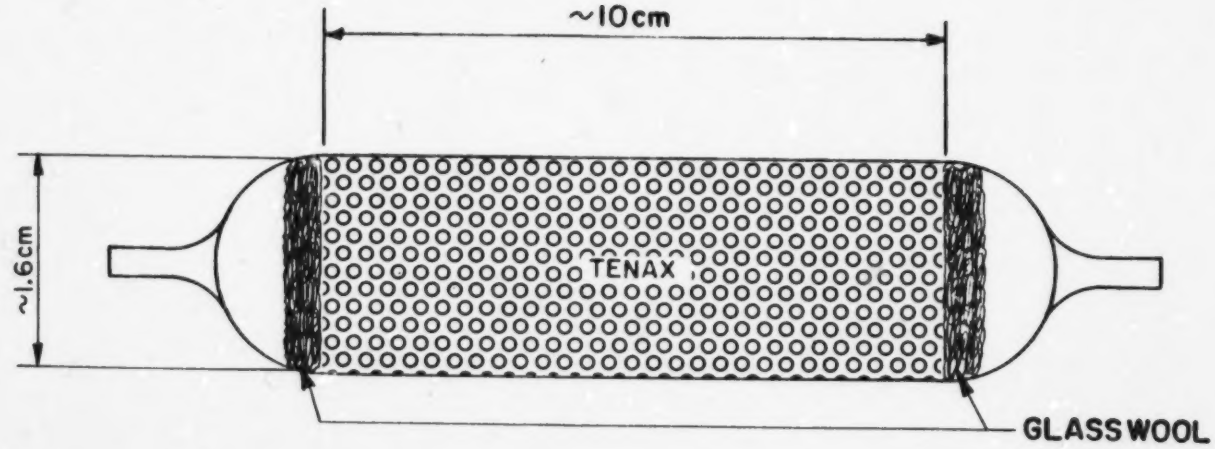


FIGURE 4

INSIDE - INSIDE VOST CARTRIDGE

5.5.3.1 Inside/Outside Type Sorbent Cartridge - A diagram of an I/O type sorbent cartridge is shown in Figure 3. In this design, the sorbent materials are held in the glass tube with a fine mesh stainless steel screen and a C-clip. The glass tube is then placed within a larger diameter glass tube, and held in place using Viton O-rings. The purpose of the outer glass tube is to protect the exterior of the resin-containing tube from contamination. The two glass tubes are held in a stainless steel cartridge holder. The ends of the glass tubes are held in place by Viton O-rings placed in machine grooves in each metal end piece. The three cylindrical rods are secured in one of the metal end pieces and fastened to the other end piece by appropriately sized nuts, thus sealing the glass tubes into the cartridge holder. The end pieces are fitted with a threaded nut onto which a threaded end cap, fitted with a Viton O-ring seal, is placed to protect the resin from contamination during transport and storage.

5.5.3.2 Inside/Inside Type Sorbent Cartridge - A diagram of an I/I type sorbent cartridge is shown in Figure 4. This cartridge is a single glass tube (10 cm by 1.6 cm I.D.) which has the ends reduced in size to accommodate a 1/4 or 3/8-inch Swagelok or Cajon gas fitting. The resin is held in place by glass wool at each end of the resin layer. The amounts of each type of sorbent material used in the I/I design are the same as for the I/O design. Threaded end caps are placed on the sorbent cartridge after packing with sorbent to protect the sorbent from contamination during

storage and transport. Care should be exercised in the placement of the threaded end cap; the male threaded fitting should be backed about 1 mm from the end of the tube prior to tightening to prevent crushing or chipping of the end of the tube.

5.6 Impinger

5.6.1 The impinger which is used to collect aqueous condensate shall have a liquid volume of 125 ml and shall be capable of providing a leak-free seal to the outlet of the Tenax sorbent cartridge. The silica gel drying tube should have sufficient capacity for at least 20 to 30 grams of silica gel.

5.7 Metering System

5.7.1 The metering system for VOST shall consist of: vacuum gauges, a leak-free pump (Thomas Model 107 or equivalent), a calibrated rotameter (Linde Model 150 or equivalent) for monitoring the gas flow rate, a dry gas meter with 2 percent accuracy (7) at the required sampling rate, and related valves and equipment. The dry gas meter shall indicate 1 liter of gas volume for each revolution of the dial. Users of VOST have suggested that the rotameter does not need to be calibrated, but a calibrated rotameter serves as a useful verification of the volume measurement from the dry gas meter.

5.7.2 Provisions will be made for monitoring the temperature of the sample gas stream between the first condenser and first sorbent cartridge. This can be done by placing a thermocouple on the

exterior glass surface of the outlet from the first condenser. The temperature at that point shall be less than 20°C. If it is not, an alternative system, providing increased cooling capacity, must be used.

5.8 Sample Transfer Lines

5.8.1 All sample transfer lines connecting the probe to VOST shall be less than 5 feet in length, if possible, and shall be heat-traced Teflon (to maintain a temperature of at least 130°C in the gas stream) with connecting fittings which are capable of forming leak-free, vacuum-tight connections without the use of sealing grease. All other sample transfer lines used with the VOST (e.g., to connect impinger with second condenser) will be Teflon with connecting fittings that are capable of forming leak-free, vacuum-tight connections without the use of sealing grease.

6. REAGENTS AND MATERIALS

6.1 Tenax, 35/60 Mesh (2,6-Diphenylene Oxide Polymer)

6.1.1 The new Tenax is Soxhlet extracted for 24 hours with methanol (Burdick & Jackson, pesticide grade or equivalent). The Tenax is dried for 6 hours in a vacuum oven at 50°C before use. Users of I/O and I/I sorbent cartridges have used slightly different thermal conditioning procedures. Although strict equivalence of the procedure has not been demonstrated, these methods have produced results that meet method quality assurance requirements (Part B, Section 7.4). I/O sorbent cartridges packed with Tenax are thermally conditioned by flowing organic-free nitrogen

30 ml/min through the resin while heating to 250°C for 8 hours. Sorbent cartridges of the I/I design packed with Tenax are thermally conditioned for 12 to 16 hours by flowing organic-free nitrogen (30 ml/min) through the resin while heating to 190°C. After thermal conditioning, the sorbent cartridges shall be stored for 24 hours at room temperature prior to monitoring the cartridges for residual organic contamination (see Section 7.4). The use of pentane to extract new Tenax and charcoal to remove non-polar impurities is not recommended. (Users have experienced problems with residual pentane in the sorbents during analysis, and therefore, this procedure is not recommended.)

6.1.2 If very high concentrations of organic compounds have been collected on the resin (e.g., micrograms of analytes), the sorbent may require Soxhlet extraction as described above. Previously used Tenax cartridges are thermally reconditioned by the method described above.

6.2 Charcoal (SKC Lot 104 Petroleum Base or Equivalent)

6.2.1 New charcoal is prepared as described in 6.1.1 above. Due to possible problems with charcoal contamination, new charcoal should be used. Users of VOST have restricted the types of charcoal used in sorbent cartridges to only petroleum-based types. Criteria for other types of charcoal are currently under development. Other types of charcoal are acceptable if recovery of POHC in laboratory evaluations meet the criteria (±50 percent) of the method (Part B, Section 7).

6.3 Viton O-Ring

6.3.1 All O-rings used in VOST shall be Viton. Prior to use, these O-rings shall be thermally conditioned in a vacuum oven at 200°C for 48 hours. O-rings will be stored in clean, screw capped glass containers prior to use.

6.4 Glass Tubes/Condensers

6.4.1 The glass resin tubes and condensers shall be cleaned with a non-ionic detergent in an ultrasonic bath, rinsed well with organic-free water and dried at 110°C. Resin tubes of the I/O design should be assembled as described in Section 7 prior to storage. Resin tubes of the I/I design shall be stored in glass containers with Teflon lined screw caps. Condensers shall be capped with appropriate end caps prior to use.

6.5 Metal Parts

6.5.1 The metal parts (e.g., stainless steel carriers, C-clips, end plugs), used in either the I/O or I/I cartridge design, are cleaned by ultrasonication in a warm non-ionic detergent solution, rinsed with reagent water, air dried and heated in a muffle furnace for 2 hours at 400°C.

6.6 Silica Gel - - Indicating Type, 6-16 Mesh

6.6.1 New silica gel may be used as received. Silica gel which has been previously used shall be dried for 2 hours at 175°C.

6.7 Crushed Ice

6.7.1 Crushed ice from any source may be added to the coolant in the reservoir.

6.8 Water

6.8.1 Water used for leak checking resin cartridges and rinsing glassware shall be reagent (see Part B, Section 5.1); water used for cooling train components in the field may be tap water.

6.9 Glass Wool

6.9.1 Glass wool shall be Soxhlet extracted for 8 to 16 hours using pentane, and oven dried at 110°C before use. The glass wool shall be checked prior to use to ensure that it does not contain residual pentane. If all pentane cannot be removed, an alternate solvent such as methanol may be used.

6.10 Nitrogen

6.10.1 Nitrogen gas will be organic-free (Linde-Union Carbide, 99.999% pure, hydrocarbon-free, or equivalent). In-line moisture traps, 5A° molecular sieve adsorbent tubes, or cryogenic traps may be used to ensure purity.

7. ASSEMBLY AND CONDITIONING OF VOST SORBENT CARTRIDGES

7.1 Introduction

7.1.1 This section describes assembly of the sorbent cartridges and procedures for storage and transport of assembled cartridges.

The assembly and packing of the sorbent cartridges should be carried out in an area free of volatile organic material. This is preferably done in a laboratory in which no organic solvents are handled or stored, and in which the laboratory air is charcoal filtered. Alternatively, the assembly procedure can be conducted in a glove box or glove bag which can be purged with organic-free nitrogen.

7.2 Assembly of Tenax Cartridges

7.2.1 The Tenax, glass tubes and metal cartridge parts are cleaned and stored according to the procedures described in Section 6. Approximately 1.6 grams of Tenax is weighed and packed into the sorbent tube which has a stainless steel screen and C-clips (I/O design) or by glass wool (I/I design) in the downstream end. The Tenax is held in place by inserting a stainless steel screen and C-clips in the upstream end (I/O design) or glass wool (I/I design). The cartridges are assembled in the metal holders (Section 5.5) and leak checked by putting on one of the end caps and pressurizing the cartridge to 30 psi with organic-free nitrogen and immersing the cartridge in distilled water to check for the appearance of bubbles. Cartridges which are determined to be leak-free are then conditioned as described in Section 7.4.

7.2.2 Assembled and conditioned resin tubes of the I/O design are placed in ice water for storage and transport. Conditioned resin tubes of the I/I design are capped and placed in ice water

for storage and transport. Limited experience by VOST users for storing and transporting resin tubes of the I/I design indicates that these tubes may be stored and transported in screw capped culture tubes placed in a clean glass or metal container which contains clean charcoal. The storage container is kept cold using ice or cold pack storage. Storage containers shall be kept in an area free from sources of organic contamination. The need for these precautions is dependent upon the user's ability to maintain blank cartridges free from contamination during storage and transport.

7.3 Assembly of Tenax/Charcoal Cartridges

7.3.1 The Tenax, charcoal and metal cartridge parts are cleaned and stored according to the procedures described in Section 6. The tubes are packed with approximately a 3:1 volume ratio of Tenax and charcoal (approximately 1 gram of each). The cartridge is assembled such that the inlet side during sampling collection is Tenax, followed by a layer of charcoal at the outlet side of the sorbent cartridge. The Tenax and charcoal are held in place by the stainless steel screens and C-clips (I/O design) or by glass wool (I/I design). The glass tubes of the I/O design containing the Tenax and charcoal are then leak checked as described in Section 7.2, checked for quality assurance as described in Section 7.4, and placed in the metal carriers according to the procedures outlined in Section 5.5. The end caps are placed on the assembled cartridges, and the assembled cartridges are placed

in ice water for storage and transport as described in Section 7.2. Glass tubes of the I/I design are leak checked as described in Section 7.2, and conditioned as described in Section 7.4. The end caps are placed on the assembled cartridges, and they are placed in a suitable container for storage and transport as described in Section 7.2.

7.4 Sorbent Cartridge Quality Assurance

7.4.1 This section describes two methods which can be used to verify that the sorbent cartridges (Tenax and Tenax/charcoal) are free from background contamination prior to sample collection.

7.4.2 The gas chromatograph with flame ionization detector is calibrated using direct injection of propane standards at the appropriate concentrations. The chromatographic column shall be 1.8 m x 0.25 cm I.D., stainless steel or glass packed with 1% SP-1000 on Carbopack (60/80 mesh) or equivalent. Following assembly and leak checking of the sorbent cartridges, they are connected to a source of organic-free nitrogen. Nitrogen is passed through each trap at a flow rate of at least 30 ml/min, while the traps are heated to 200°C. The effluent from the trap is monitored with a flame ionization detector to check for emission of volatile organic compounds from the cartridge. The conditioning is continued until the amount of total chromatographable organics is below 0.2 ng as propane.

7.4.3 The gas chromatograph with flame ionization detector is calibrated by analyzing a Tenax cartridge which has been spiked with 175 ng benzene, 175 ng toluene and 150 ng bromofluorobenzene (BFB). The cartridge is spiked using the solvent-flush technique (see Part B, Section 6.2.3). The chromatographic conditions shall be the same as those described in Part B, or shall demonstrate the capability of identifying background levels of volatile POHCs with the required sensitivity. Following assembly and leak checking, the sorbent cartridge(s) is placed in the desorption heater for 10 minutes with a helium flow of 50 ml/min. The effluent from the cartridge is passed through a trap filled with glass beads which is cooled in liquid nitrogen. (If a pair of Tenax and Tenax/charcoal cartridges are monitored in a single desorption run, the Tenax/charcoal cartridge should be upstream ofthe Tenax cartridge.) At the end of the 10-minute desorption period, the glass bead filled trap is heated, the carrier gas flow directed to a gas chromatograph equipped with flame ionization detector and chromatographic column suitable for volatile organic analysis (see Part B, Section 4.3.2). Blank sorbent cartridges which are monitored using this technique shall contain less than 2 ng total chromatographable organics (as benzene or toluene). If in using this procedure the background exceeds 10 ng (as benzene or toluene), the cartridges must be recleaned and reanalyzed.

8. SAMPLE COLLECTION PROCEDURE

8.1 Pretest Preparation

8.1.1 All train components shall be cleaned and assembled as described in Sections 5, 6, and 7. The dry gas meter shall have

been calibrated within 30 days prior to use. All field data shall be recorded on a Field Data Sheet (or field notebook). An example of a Field Data Sheet for VOST is shown in Figure 5.

8.2 VOST Assembly

8.2.1 The VOST is assembled according to the schematic diagram in Figure 2. Cooling water is circulated to the condensers and the temperature of the cooling water shall be maintained near 0°C. The end caps of the sorbent cartridges will be placed in a clean screw capped glass container during sample collection. The condensate pot shall not be immersed in ice water.

8.3 Leak Checking

8.3.1 The train is leak checked by closing the valve at the inlet to the first condenser and pulling a vacuum equivalent to 10 inches Hg (250 mm Hg) above the system's operating pressure. The traps and condensers are isolated from the pump and the leak rate noted. The system shall hold at 10 inches Hg above the system operating pressure with no discernible leakage (pressure increase of less than 0.1 inches Hg/min). If the leak check does not meet specifications, the cause of the problem must be identified and corrected and leak check repeated. After leak checking, the train should be returned to atmospheric pressure by attaching a charcoal filled tube to the isolation valves above the first condenser and opening the valve to admit air to the train through the charcoal filter. These procedures will minimize contamination of VOST train components by excessive exposure to the fugitive emissions at hazardous waste incinerator sites.

Plant_____ Stack No._____

Date_____ Probe No._____

Location_____ VOST No._____

Operator_____ Rotameter No._____

Field Blank I.D.: Tenax_____ Dry Gas Meter No._____

Tenax/Charcoal_____

Pair No.[b]	Leak Check	Cartridge I.D.		Rotameter Reading (l/min)	Time		Sampling Duration (min)	Probe Temp. (°C)	Barometric Pressure (in of Hg)	Condenser Outlet Temp. (°C)	Meter Temp. (Outlet)	Dry Gas Meter		Gas Sample Volume (liters)	Comments
		Tenax	Tenax/ Charcoal		Initial	Final						Initial	Final		

Condensate Samples:

Run No.	Sample I.D.	Comments

NOTES: [a]Reading should be tabulated at the beginning of a run and every five minutes thereafter.
[b]Refers to sample collection on one pair of Tenax and Tenax/charcoal traps.

FIGURE 5. VOST FIELD DATA SHEET[a]

8.3.2 After leak checking but before the initiation of sample collection, the probe shall be purged with stack gas. This can be accomplished by attaching a pump to the isolation valve above the first condenser and drawing stack gas through the probe via the isolation valve, so that at the initiation of sample collection the probe is purged of ambient air.

8.4 Sample Collection

8.4.1 Prior to the initiation of sample collection, the probe shall be located in the stack at a point of average stack gas velocity and temperature. (These values can be determined using the procedures described in References 6 and 7.) Care should be exercised in the location of the probe in the stack to minimize effects of dilution air which may enter the stack through the sampling port and thereby impair the collection of a representative sample of the stack gas.

8.4.2 After leak checking (see Section 8.3.1), sample collection is accomplished by opening the valve at the inlet to the first condenser, turning on the pump, and sampling at a rate of 1 liter/minute for 20 minutes. The volume of sample for any pair of traps shall not exceed 20 liters. The temperature of the gas stream at the inlet to the first sorbent cartridge must be maintained at or below 20°C during sample collection (see Section 5.6.2).

8.4.3 After the collection of 20 liters of sample, the train is leak tested using the procedures described in Section 8.3. If this post leak test criterion is not met, the samples shall not be analyzed. If leak check criterion is met, the train is returned to atmospheric pressure as described in Section 8.3.1, the two sorbent cartridges removed, the end caps replaced, and the cartridges returned to a suitable container for storage and transport until analysis (see also Section 7.2.2).

8.4.4 In some cases, there may be a requirement to analyze the aqueous condensate. This situation may arise for water soluble volatile organic compounds. For these situations, preliminary laboratory evaluation of the sampling and recovery efficiency (including the purging efficiencies of the compounds) must be performed (Part B, Sections 7 and 11). Sampling and analysis procedures for water soluble volatile organics are currently being developed. In this case, when a pair of sorbent cartridges is changed, duplicate samples of the aqueous condensate should be poured into 40 ml glass vials equipped with plastic screw caps (Pierce 13075 or equivalent), and Teflon-faced silicon septa (Pierce 12722 or equivalent). If insufficient condensate is available, the vials shall be topped off with reagent water. The vials shall be carefully filled just to overflowing so that no air bubbles pass through the sample as the vial is being filled. The vial shall be sealed so that no air bubbles are entrapped in it. Vials shall be stored and transported at ice or cold pack temperature.

8.4.5 A new pair of cartridges is placed in the VOST. The VOST leak checked as described in Section 8.3 and the sample collection process repeated as described above. Sample collection continues until six pairs of cartridges have been taken (see Section 2.3). A maximum of six pairs of cartridges may be taken over a 2-hour sampling period (see Section 2.3).

8.4.6 All sample cartridges shall be stored on cold packs or ice until ready for analysis.

8.5 Field, Trip and Laboratory Blanks/Aqueous Field Blanks

8.5.1 Field Blanks - Blank Tenax and Tenax/charcoal cartridges are taken to the sampling site and the end caps removed for the period of time required (approximately 5 minutes) to exchange two pairs of cartridges on VOST. After the two VOST cartridges have been exchanged, the end caps are replaced on the blank Tenax and Tenax/charcoal tubes. These are returned to appropriate storage (see Section 7.2.2) and analyzed with the sample cartridges. At least one pair of field blanks (one Tenax, one Tenax/charcoal) shall be included with each six pairs of sample cartridges collected (or for each field trial using VOST to collect volatile POHCs). It is advisable to use two pairs of field blanks for each six pairs of cartridges collected.

8.5.2 Trip Blanks - At least one pair of blank cartridges (one Tenax, one Tenax/charcoal) shall be included with the shipment of cartridges to a hazardous waste incinerator site. These trip

blanks will be treated as any other cartridges except that the end caps will not be removed during storage at the site. This pair of cartridges will be analyzed to monitor potential contamination which may occur during storage and shipment. One user (5) recommended including one pair of trip blanks for each VOST run conducted during a trial burn to obtain a more meaningful basis for blank correction of sample cartridges (Part B, Section 12.1.2).

8.5.3 Laboratory Blanks - One pair of blank cartridges (one Tenax, one Tenax/charcoal) will remain in the laboratory using the method of storage for field samples. If the field and trip blanks contain high concentrations of contaminants (e.g., greater than 2 ng of a particular POHC), the laboratory blank shall be analyzed in order to identify the source of contamination.

8.5.4 Aqueous Field Blanks - If the aqueous condensate is to be analyzed for volatile POHCs, an aqueous field blank is required. This consists of duplicate samples of reagent water placed in vials described in Section 8.4.3. These vials shall be stored and shipped in the same way as empty vials/aqueous condensate samples, and should be analyzed at the same time as the aqueous condensate samples. Additionally, a reagent water sample (prepared as above) will be retained in storage in the laboratory. If the analysis of aqueous field blanks shows the presence of POHCs, the corresponding laboratory blank shall be analyzed to verify that the residual contamination is not due to contamination of the aqueous field blanks at the time of preparation or during storage in the laboratory.

PART B

PROTOCOL FOR ANALYSIS OF SORBENT CARTRIDGES

FROM VOLATILE ORGANIC SAMPLING TRAIN

1. SCOPE AND APPLICABILITY

1.1 This method covers the analysis of volatile POHCs collected on Tenax and Tenax/charcoal sorbent cartridges using a VOST. Much of the description for purge-trap-desorb (P-T-D) GC/MS analysis is included in References 8 and 9. Since the majority of gas streams sampled using VOST will contain a high concentration of water, the analytical method is based on the quantitative thermal desorption of volatile POHCs from the Tenax and Tenax/charcoal cartridges and analysis by P-T-D GC/MS in order to minimize the effects of water on the analysis. This method is applicable to organic compounds with boiling points between 30° and 100°C. Many compounds with boiling points below 30°C and between 100° and 150°C, may be efficiently collected and analyzed using this method. However, laboratory evaluation of the collection and recovery efficiency for compounds with boiling points outside the range of 30° to 100°C (or those for which no VOST data are available) shall be performed (see Section 7).

1.2 This method is applicable to the analysis of Tenax and Tenax/charcoal cartridges used to collect volatile POHCs from wet stack gas effluents from hazardous waste incinerators.

1.3 The sensitivity of the analytical method for a particular volatile POHC depends on the level of interferences, the presence of detectable levels of volatile POHCs in blanks, and the ability to purge the volatile POHCs from water. The target detection limit for the method is 0.1 $\mu g/m^3$ (0.1 ng/l) in the stack gas. This corresponds to 2.0 ng adsorbed on a single pair of Tenax and Tenax/charcoal cartridges. Since 2 ng of a POHC may not be detectable by P-T-D GC/MS analysis, the method is designed to permit thermal desorption of up to five pairs of Tenax and Tenax/charcoal cartridges onto a single pair for analysis in order to achieve the target detection limit of the method. For a POHC present in the gaseous effluent at a concentration of 0.1 $\mu g/m^3$ (0.1 ng/l), the desorption of multiple pairs of cartridges onto a single pair for analysis can provide a total of 10 ng for analysis by P-T-D GC/MS.

1.4 This method is recommended for use only by experienced analytical chemists or under the close supervision of such qualified persons.

2. SUMMARY OF METHOD

2.1 A schematic diagram of the analytical system is shown in Figure 6. Pairs of the sorbent cartridges are spiked with an internal standard and thermally desorbed for 10 minutes at 180°C with organic-free nitrogen gas (at a flow rate of 100 ml/min), bubbled through 5 ml of organic-free water, and trapped on an analytical sorbent trap. After the 10-minute desorption, the

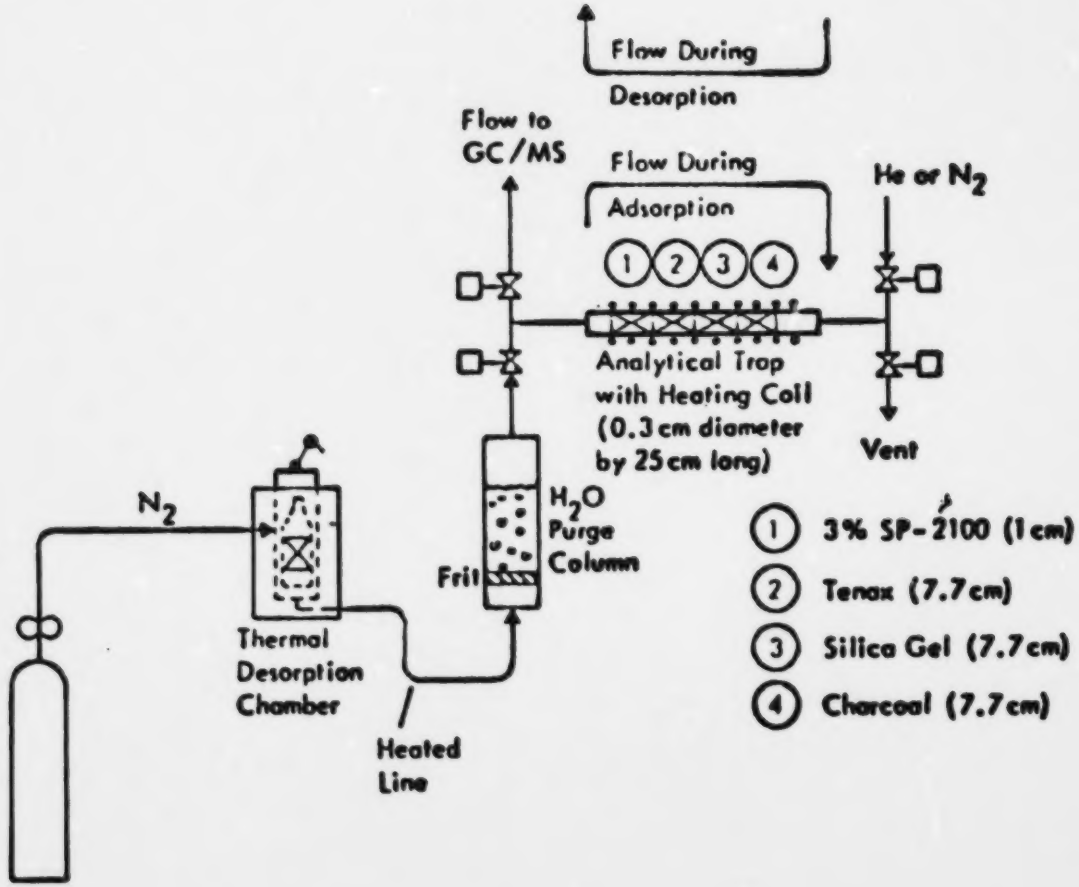


FIGURE 6

SCHEMATIC DIAGRAM OF TRAP DESORPTION

/ANALYSIS SYSTEM

analytical sorbent trap is rapidly heated to 180°C with the carrier gas flow reversed so that the effluent flow from the analytical trap is directed into the GC/MS. The volatile POHCs are separated by temperature programmed gas chromatography and detected by low resolution mass spectrometry. The concentrations of volatile POHCs are calculated using the internal standard technique. To achieve increased sensitivity, multiple pairs of cartridges (up to five pairs) may be desorbed onto a single pair of Tenax and Tenax/charcoal cartridges. The resulting pair is analyzed by P-T-D GC/MS.

3. PRECISION AND ACCURACY

3.1 The overall accuracy of sample collection and analysis using VOST has been determined in laboratory evaluations to average ±50 percent for analysis of three replicate cartridges (5). These values may be revised as further evaluation of VOST performance is conducted.

3.2 The precision for the internal standard response (area) should be 20 percent during any given analysis period at a particular multiplier voltage of the mass spectrometer.

4. APPARATUS

4.1 Thermal Desorption Unit

4.1.1 The thermal desorption unit (Nutech Corporation Model 320 or equivalent) shall be capable of thermally desorbing the sorbent

resin tubes. It shall be capable of rapidly heating the tubes to 180°C±10°C with flow of organic-free nitrogen through the tubes.

4.2 Purge and Trap Unit

4.2.1 The purge and trap unit consists of three separate pieces of equipment: the sample purger, analytical sorbent trap and the desorber. It should be capable of meeting all requirements of Sections 5.2 thru 5.2.4 of EPA Method 624 for analysis of purgeable organic compounds from water (8, 9). The analytical trap as specified in EPA Method 624 consists of 3% SP-2100, Tenax, silica gel, charcoal. Some users have found that improved performance can be achieved using only Tenax and charcoal in the analytical sorbent trap (5).

4.3 GC/MS System

4.3.1 Gas Chromatograph - An analytical system complete with a temperature programmable GC suitable for on-column injection, and all required accessories including syringes, analytical columns, and gases.

4.3.2 Column - Column dimensions shall be 1.8 m long by 0.25 cm I.D., stainless steel or glass, packed with 1% SP-1000 on Carbopack B (60/80 mesh) or equivalent.

4.3.3 Mass Spectrometer - Capable of scanning from 20 to 260 amu every 7 seconds or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass

spectrum which meets all criteria described in Method 624 when 50 ng of 4-bromofluorobenzene (BFB) is injected through the GC inlet.

4.3.4 GC/MS Interface - Any GC to mass spectrometer interface that gives acceptable calibration points at 50 ng or less per injection for each of the parameters of interest and achieves all performance criteria of Method 624 may be used. GC to mass spectrometer interfaces constructed of all-glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichloro-dimethylsilane.

4.3.5 Data System - A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

5. REAGENTS

5.1 Reagent Water

5.1.1 Reagent water is defined as water in which an interferent is not observed at the detection limit of the parameters of interest.

5.1.2 Reagent water may be generated by passing tap water through a carbon filter bed containing about 450 grams of activated carbon (Calgon Corporation, Filtrasorb-300 or equivalent).

5.1.3 Reagent water may also be prepared by boiling distilled water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free, inert gas through the water for one hour. While still hot, the water should be transferred to a narrow mouth, screw cap bottle and sealed with a Teflon lined septum and cap.

5.1.4 Other methods which can be shown to produce reagent water can be used.

5.2 Analytical Trap Reagents

a) Tenax (60/80 mesh) - Chromatographic grade or equivalent

b) Methyl silicone packing - 3% OV-1 on Chromosorb W (60/80 mesh) or equivalent

c) Silica gel, Davison Chemical (35/00 mesh), Grade 15 or equivalent

d) Charcoal, petroleum based (SKC Lot 104 or equivalent) (see Section 6.2 in Part A)

5.3 Stock Standard Solution

5.3.1 Stock standard solutions will be prepared from pure standard materials or purchased certified solutions. The stock standards should be prepared in methanol using assayed liquids or gases as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be used when the analyst handles high concentrations of such materials.

5.3.2 Fresh standards should be prepared weekly for volatile POHCs with boiling points of <30°C. All other standards must be replaced monthly, or sooner if comparison with check standards indicates a problem.

5.4 Secondary Dilution Standards

5.4.1 Using stock standard solutions, prepare secondary dilution standards in methanol which contain the compounds of interest either singly or mixed together, and at concentrations such that the desorbed calibration standards will bracket the working range of the analytical system.

5.5 Bromofluorobenzene (BFB) Standard

5.5.1 Prepare a 25 µg/ml solution of BFB in methanol.

5.6 Deuterated (d_6) Benzene Standard

5.6.1 Prepare a 25 µg/ml solution in methanol.

6. CALIBRATION

6.1 Assembly of P-T-D Device

6.1.1 Assemble a purge and trap desorption device (P-T-D) which meets all the requirements of Section 10.2 of this protocol and Section 5.2 of USEPA Method 624 (3).

6.1.2 Connect the thermal desorption device to the purge and trap device. Calibrate the P-T-D GC/MS system using the internal standard technique (Section 6.2).

6.2 Internal Standard Calibration Procedure

6.2.1 This approach requires the use of deuterated benzene as the internal standard for these analyses. Other internal standards may be proposed for use in certain situations. The important criteria for choosing a particular compound as an internal standard are that it be similar in analytical behavior to the compounds of interest, and it can be demonstrated that the measurement of the internal standard is not affected by method or matrix interferences. Other internal standards which have been used are d_{10}-ethylbenzene and d_4-1,2-dichloroethane. Several users add 50 ng of BFB to all sorbent cartridges (in addition to one or more internal standards) to provide continuous monitoring of the GC/MS performance relative to BFB.

6.2.2 Prepare calibration standards at a minimum of three concentration levels for each analyte of interest. The calibration standards are prepared by spiking a blank Tenax or Tenax/charcoal

cartridge with a methanolic solution of the calibration standards (including 50 ng of the internal standard, such as deuterated benzene) using the flash evaporation technique.

6.2.3 The cartridge shall be mounted in the gas chromatograph so that the carrier gas enters the cartridge in the same direction as during sample collection (which is opposite to the direction of gas flow during P-T-D GC/MS analysis). The glass cartridge should be attached to the injection port of a gas chromatograph. The injector temperature is maintained at 160°C, and the carrier gas flow through the cartridges should be maintained at about 50 ml/min.

6.2.4 The flash evaporation technique requires filling the needle of a 5.0 (µl) syringe with clean methanol and drawing air into the syringe until the tip of the plunger reaches the 1.0 µl mark. This is followed by drawing a methanolic solution of the calibration standards (containing 25 µg/µl of the internal standard) until the tip of the plunger reaches the 3.0 µl mark. The contents of the syringe should be slowly expelled through the gas chromatograph injection port over about 15 seconds. After 25 seconds have elapsed, the gas flow through the cartridge should be shut off, the syringe removed, and the cartridge analyzed by the P-T-D GC/MS procedure outlined in Section 10.2. The total flow of gas through the cartridges during addition of calibration standard to blank cartridges, or internal standards to sample cartridges, should be 25 ml or less to avoid breakthrough of volatile sample components.

6.2.5 Analyze each calibration standard on both Tenax and Tenax/charcoal cartridges according to Section 10. The calibration procedures shall be identical to those used for analysis of sample cartridges. If cartridges are analyzed separately, then the Tenax and Tenax/charcoal cartridges must be calibrated separately. The direction of carrier gas flow through the cartridges during the desorption step should be opposite from the gas flow through the cartridge during sample collection so the inlet side of the cartridge during sample collection becomes the outlet side during P-T-D analysis. Tabulate the area response of the characteristic ions of each analyte against the concentration of the internal standard and calculate response factor (RF) for each compound using Equation 1.

$$RF = A_S C_{is} / A_{is} C_s \qquad [1]$$

where A_s = Area of the characteristic ion for the analyte to be measured

A_{is} = Area of the characteristic ion for the internal standard

C_{is} = Amount (ng) of the internal standard

C_s = Amount (ng) of the volatile POHC in calibration standard

If the RF value over the working range is a constant (<10% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_S/A_{is} versus RF.

6.2.6 The working calibration curve or RF must be verified on each working day by the measurement of one or more of the calibration standards. If the response varies by more than ±25%, new calibration standards must be prepared and analyzed.

7. QUALITY CONTROL

7.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of blank Tenax and Tenax/charcoal cartridges spiked with the analytes of interest. The laboratory shall demonstrate collection and/or recovery efficiencies for compounds with boiling points outside the 30° to 100°C range, which meet the method criteria, prior to field use of the VOST (Part A, Section 3.2). The laboratory is required to maintain performance records to define the quality of data which are generated. Ongoing performance checks mus be compared with established performance criteria to determine if results are within the expected precision and accuracy limits of the method. (Note: NBS traceable audit cylinders are being developed by Research Triangle Institute under the direction of USEPA-EMSL, Research Triangle Park, NC. The cylinders may be used for performance trials and evaluation of collection and recovery efficiencies in lieu of the methods specified in this section.)

7.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable precision and accuracy with this method. This ability is established as described in Section 7.2.

7.1.2 Recovery data for compounds boiling between 100° and 150°C must be provided which meets the method criteria (see Section 7.2.2). Laboratory evaluation is required in lieu of that data. The method of evaluation is that specified in Section 7.2 with the exception that it is not required to pull 20 liters of organic-free nitrogen through the sorbent cartridges.

7.1.3 Laboratory evaluation of collection and recovery efficiencies shall be performed for compounds with boiling points below 30°C. Due to the possibility of sample breakthrough and poor recovery of the sample from the charcoal, the evaluation shall be comparable to that described in Reference 5. A gas stream containing the POHC shall be generated and sampled using the VOST. The sampling rate for the laboratory evaluation shall be the same as that proposed for field application. The laboratory evaluation must meet the precision and accuracy criteria described in Section 7.2.2.

7.1.4 The laboratory must spike all Tenax and Tenax/charcoal cartridges with the internal standard(s) to monitor continuing laboratory performance. This procedure is described in Section 6.2.

7.2 To establish the ability to generate acceptable accuracy and precision, the analyst must spike blank Tenax and Tenax/charcoal with the analytes of interest at two concentrations in the working range by the flash vaporization technique discussed in Sections 6.2.3 and 6.2.4. The cartridges are removed from the gas chromatograph and connected to a source of organic-free nitrogen. The cartridges sample 20 liters of nitrogen at a flow rate equivalent to that proposed for field use of VOST.

7.2.1 The average response factor (RF) and the standard deviation (S) for each must be calculated.

7.2.2 The average recovery and standard deviation must fall within the expected range for determination of volatile POHCs using this method. The expected range for recovery (indicative of accuracy) of volatile POHCs using this method is ±50 percent. The expected standard deviation is 25 percent.

7.3 The analyst must calculate method performance criteria for the internal standard.

7.3.1 Calculate upper and lower control limits for method performances using the average area response (A) and standard deviation (S) for internal standard:

Upper Control Limit (UCL) = A + 3S

Lower Control Limit (LCL) = A - 3S

The UCL and LCL can be used to construct control charts which are useful in observing trends in performance. The control limits must be replaced by method performance criteria as they become available from the USEPA.

7.4 Each day, the analyst must demonstrate through analysis of blank Tenax and Tenax/charcoal cartridges and reagent water that interferences from the analytical system are under control.

8. SAMPLE COLLECTION, PRESERVATION AND HANDLING

8.1 The requirements for sample collection, preservation, and handling are described in Part A of this protocol.

9. DAILY GC/MS PERFORMANCE TESTS

9.1 The daily GC/MS performance tests required for this method are described in Section 10 of EPA Method 624 (9). The key abundance criteria for BFB which must be met before any samples are analyzed are listed below. This can be done by injecting 50 ng of BFB directly on the column or by adding 50 ng of BFB to a blank Tenax sorbent cartridge (see Sections 6.2.3 and 6.2.4) and desorbing this cartridge according to the procedures described in Section 10. The latter procedure is preferred when all sample sorbent cartridges are spiked with BFB in addition to one or more of the internal standards discussed in Section 6.2.1.

BFB KEY ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95
173	<2% of mass 174
174	>50% of mass 95
175	5 to 9% of mass 174
176	>95% but <101% of mass 174
177	5 to 9% of mass 176

10. SAMPLE DESORPTION AND GAS CHROMATOGRAPHY

10.1 The P-T-D GC/MS procedures are those described in Section 11 of Method 624 (9) with the addition of the procedure described in Section 10.2 for desorption of Tenax and Tenax/charcoal cartridges.

10.2 The schematic of the P-T-D GC/MS system is shown in Figure 6. The sample cartridge is placed in the thermal desorption apparatus (Nutech 320 or equivalent) and desorbed in the P-T-D system by heating to 180°C for 10 minutes. Sample cartridges may be desorbed in pairs. However, if the analyte concentrations are anticipated to be sufficiently high to saturate the GC/MS when desorbed in pairs, consideration should be given to individual analysis of cartridges. The desorbed components pass into the bottom of the water column, are purged from the water and

collected on the analytical sorbent trap. After the 10-minute desorption period, the compounds are desorbed from the analytical sorbent trap into the GC/MS system according to the procedures described in Section 11 of Method 624.

11. AQUEOUS CONDENSATE

11.1 Analysis of aqueous condensate samples should be performed according to the procedures described in References 8 and 9. If the volatile POHCs of interest are water soluble, it is necessary to demonstrate that this method is capable of recovery of the volatile POHCs of interest using Method 624. This can be accomplished by P-T-D GC/MS analysis of reagent water which has been fortified with the analytes of interest.

11.2 If adequate recovery of water soluble volatile POHCs cannot be achieved using the procedures described in References 8 and 9, alternative methods for analysis, such as direct aqueous injection, may be required. If an alternative analytical method is used, method performance must be documented by analysis of laboratory reagent water which has been fortified with the volatile POHCs of interest.

11.3 Methods for analysis of water soluble volatile POHCs in aqueous condensate are currently under development.

12. QUALITATIVE IDENTIFICATION

12.1 The qualitative identification procedure of volatile POHCs using this protocol is described in Section 12 of Method 624 (9).

13. CALCULATIONS

13.1 When an analyte has been qualitatively identified, quantification should be based on the integrated abundance from the EICP of the primary characteristic ion chosen for that analyte. If the sample produces an interference for the primary characteristic ion, a secondary characteristic ion should be used.

13.1.1 Using the internal standard calibration procedure, the amount of analyte in the sample cartridge is calculated using the response factor (RF) determined in Section 6.2.5 and Equation 2.

$$\text{Amount of POHC} = A_s C_{is} / A_{is} RF \qquad [2]$$

where A_s = Area of the characteristic ion for the analyte to be measured

A_{is} = Area for the characteristic ion of the internal standard

C_{is} = Amount (ng) of internal standard

13.1.2 The choice of methods for evaluating data collected using VOST for incinerator trial burns is a regulatory decision. The procedures used extensively by one user are outlined below (10).

13.1.3 The total amount of the POHCs of interest collected on a pair of traps should be summed. These values should then be blank corrected. Guidelines for blank correction of sample cartridges are outlined below.

13.1.3.1 After all blanks (field and trip) are analyzed, a paired t-test should be used to determine whether trip blanks are significantly different from field blanks. If no difference is found, then the mean and standard deviation of the combined field and trip blanks for each POHC of interest is calculated, and that value is used as the blank.

13.1.3.2 If, using the paired t-test, the field and trip blanks are determined to be different, then the field blank (or the mean of multiple field blanks) associated with a particular run should be used as the blank value for that particular run.

13.1.3.3 If an individual field blank is used as the blank value for a particular run, the VOST user must evaluate whether this blank is different from sample cartridges associated with this blank. Although no specific criteria are offered here for guidance in this case, specific criteria for use of individual field blanks for blank correction will be developed as more data for use of VOST becomes available. This situation can be alleviated by including two field blanks (i.e., two blank Tenax and two blank Tenax/charcoal cartridges) per run.

13.1.4 Next, for each sample/POHC combination, a determination must be made as to whether a particular sample is significantly different from the associated blank. If the mean of the trip and field blanks is used, then a sample is different from the blank if:

(measured sample value)-(mean blank value) $\geq$3

x blank standard deviation

If the sample is determined to be different from the blank according to the above criteria, then the emission value of a particular POHC is blank corrected by subtracting the mean blank value (as defined in Section 12.1.3) from the measured sample value. (If an individual field blank is used as the blank value, the above criteria do not apply.)

13.1.5 If, according to the above procedures, the sample cannot be distinguished from the blank (i.e., for a given POHC there is a high sample value and high blank value or there is a low sample value and low blank value), the measured sample value is not blank corrected. In this case, the measured sample value is used to calculate a maximum emission value (and therefore a minimum DRE value) for that particular run.

13.1.6 The observation of high concentrations of POHCs of interest in blank cartridges indicates possible residual contamination of the sorbent cartridges during shipment and use at the site. Data which fall in this category (especially data indicating high concentrations of POHCs in blank sorbent cartridges) should be qualified with regard to validity, and blank data should be reported separately. The applicability of data of this type to the determination of DRE is a regulatory decision. Continued observation of high concentrations of POHCs in blank sorbent cartridges

indicates that procedures for cleanup, monitoring, shipment and storage of sorbent cartridges by a particular user, be investigated to eliminate this problem.

13.1.7 After blank corrections have been made, the amounts of individual POHCs on each sorbent cartridge used for a given run is summed and divided by the volume of gas sampled to obtain the concentration of each POHC in the stack gas.

13.1.8 If any internal standard recoveries fall outside the control limits established in Section 7.3.1, data for all analytes determined for that cartridge(s) must be qualified with the observation.

14. METHOD PERFORMANCE

14.1 The method detection limit, average recoveries and standard deviation of the average recoveries of the analytes determined using this method have not yet been established. The method performance will be documented as more data become available.

REFERENCES
(For A and B)

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4) Harris, J. C., et al. "Sampling and Analysis Methods for Hazardous Waste Combustion," EPA 600/8-84-002, February 1984.

5) Jungclaus, G., et al. "Development of a Volatile Organic Sampling Train (VOST)," Presented at 9th Annual Research Symposium, Land Disposal, Incineration and Treatment of Hazardous Wastes, Ft. Mitchell, KY, May 2-4, 1983.

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8) Federal Register, 44, 69464, December 3, 1979.

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10) Trenholm, A. Midwest Research Institute, Personal Communication, August 5, 1983.